

Perchlorate Detection at Nanomolar Concentrations by Surface-Enhanced Raman Scattering

BAOHUA GU,* CHUANMIN RUAN, and WEI WANG

Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 (B.G., W.W.); and Oak Ridge Institute for Science and Education, Oak Ridge, Tennessee 37831 (C.R.)

Perchlorate (ClO_4^-) has emerged as a widespread environmental contaminant and has been detected in various food products and even in human breast milk and urine. This research developed a sensing technique based on surface-enhanced Raman scattering (SERS) for rapid screening and monitoring of this contaminant in groundwater and surface water. The technique was found to be capable of detecting ClO_4^- at concentrations as low as 10^{-9} M (or ~ 0.1 $\mu\text{g/L}$) by using 2-dimethylaminoethanethiol (DMAE) modified gold nanoparticles as a SERS substrate. Quantitative analysis of ClO_4^- was validated with good reproducibility by using both simulated and contaminated groundwater samples. When coupled with a portable Raman spectrometer, this technique has the potential to be used as an *in situ*, rapid screening tool for perchlorate in the environment.

Index Headings: Perchlorate; Detection limit; Surface-enhanced Raman scattering; SERS; Sensor; Groundwater; Gold nanoparticles.

INTRODUCTION

New technologies for rapid screening and quantitative analysis of perchlorate (ClO_4^-) in the environment are of great interest since perchlorate has emerged as a widespread contaminant in groundwater and surface water in the United States (US).^{1–4} Perchlorate has been detected in drinking water, plants, food products, and human urine and breast milk in many areas of the US and abroad.^{5–8} Perchlorate is manufactured primarily for use as an ingredient of solid rocket propellant and explosives but is also known to form naturally, such as that found in the hyperarid Atacama Desert in Chile.^{1–3,9–11} Recent studies also indicate that naturally forming perchlorate is more widespread than originally thought (only in the arid regions), and this explains the wide occurrences of sub-parts per billion (ppb) concentration levels of perchlorate in the environment where no anthropogenic sources are known to exist.^{10,12–14} Because of its potential health effects on thyroid function by interfering with iodide uptake, the widespread occurrence of perchlorate in the environment has generated considerable interest in its contamination source, risk assessment, and detection and remediation technologies. Perchlorate is highly soluble and exceedingly mobile in aqueous systems and can persist for many decades under typical groundwater and surface water conditions.¹⁵ Therefore, methods for rapid and sensitive assay of this contaminant are particularly useful for its monitoring and detection in the environment.

Various techniques such as ion chromatography (IC),^{14,16} electro-spray mass spectrometry (MS), IC-MS, and IC-MS-MS,^{2,17} ion-selective electrodes,^{18,19} and capillary electrophoresis^{17,20} have been well developed and are routinely used for

perchlorate detection and analysis. Currently, IC is perhaps the most commonly used technique for the analysis and screening of perchlorate in environmental samples, although IC-MS or EPA Methods 6850 and 6860 are preferred because of the specificity of MS in identifying ClO_4^- in complex environmental matrices. However, these methods are usually performed in analytical laboratories and require sample preparation and lengthy analytical time. For rapid screening and long-term monitoring, *in situ*, nondestructive, and sensitive analysis of ClO_4^- is highly preferred. Ion-selective electrodes have been developed for such purposes, but their sensitivity and selectivity remain an issue to be improved.^{17–19}

The surface-enhanced Raman scattering (SERS) technique has the potential to allow rapid, sensitive, and *in situ* detection of ClO_4^- . SERS refers to the observation that the apparent Raman cross-section for an analyte adsorbed on roughened metal surfaces (e.g., silver or gold) is enhanced by many orders of magnitude over their normal values, allowing the detection up to single molecular levels.^{21–24} The characteristic vibrational frequency of the symmetric stretch for ClO_4^- at about 950 cm^{-1} (dehydrated) and 930 cm^{-1} (in aqueous solution) also makes the technique highly selective. However, the key for this technology to be useful is the development of robust, sensitive, and reproducible SERS substrates, on which the Raman signal could be substantially enhanced. Using roughened gold electrode surfaces in a flow cell, previous studies have shown that the technique was capable of detecting ClO_4^- at 10^{-4} – 10^{-5} M concentration levels,²⁵ and recent investigations reached a detection limit of about 10^{-6} – 10^{-7} M by using surface-modified gold or silver nanoparticles as SERS substrates.^{26–29} However, improved sensitivity (e.g., $<10^{-8}$ M), reproducibility, stability, and uniformity remain significant issues before SERS can be used as a routine analytical tool for ClO_4^- detection. Additionally, the quantitative relation or linearity has been found only within limited concentration ranges of the analyte or is nonexistent because of problems associated with poor reproducibility and substrate stability.^{25,27,30–33} The surface modification, which may allow analyte to be sorbed or concentrated and distributed uniformly on a substrate, has been proposed as one of the key steps for enhancing the sensitivity, reproducibility and linearity of SERS.^{26–28,30–32} Here we report a new SERS technique for detecting ClO_4^- at concentrations as low as 10^{-9} M (or 0.1 ppb) by using 2-dimethylaminoethanethiol modified gold nanoparticles as a SERS substrate.

MATERIALS AND METHODS

All chemicals used in this experiment were of reagent grade or better. Gold chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), nitric acid (HNO_3) (70%), 2-dimethylaminoethanethiol hydrochloride (DMAE) [$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{SH} \cdot \text{HCl}$] (98%), sodium citrate

Received 4 August 2008; accepted 17 October 2008.

* Author to whom correspondence should be sent. E-mail: gub1@ornl.gov.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Perchlorate Detection At Nanomolar Concentrations By Surface-Enhanced Raman Scattering				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Oak Ridge National Laboratory,Environmental Sciences Division,Oak Ridge,TN,37831				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES Applied Spectroscopy, Volume 63, 98-102, Number 1, 2009, U.S. Government or Federal Rights License					
14. ABSTRACT Perchlorate (ClO₄) has emerged as a widespread environmental contaminant and has been detected in various food products and even in human breast milk and urine. This research developed a sensing technique based on surface-enhanced Raman scattering (SERS) for rapid screening and monitoring of this contaminant in groundwater and surface water. The technique was found to be capable of detecting ClO₄ at concentrations as low as 10⁻⁹ M (or ;0.1 lg/L) by using 2-dimethylaminoethanethiol (DMAE) modified gold nanoparticles as a SERS substrate. Quantitative analysis of ClO₄ was validated with good eproducibility by using both simulated and contaminated groundwater samples. When coupled with a portable Raman spectrometer, this technique has the potential to be used as an in situ, rapid screening tool for perchlorate in the environment.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

TABLE I. Major anionic composition of two field groundwater samples (GW-1 and GW-2) and a simulated groundwater sample (SGW).

Property	SGW	GW-1	GW-2
Perchlorate (μM)	0–1	8.3	0.01
Chloride (mM)	1.0	0.28	3.0
Sulfate (mM)	0.1	0.16	0.49
Nitrate (mM)	0.1	0.16	0.52
Phosphate (mM)	0.1	ND ^a	ND
Bicarbonate (mM)	0	2.8	3.1
pH	6.5	7.3	8

^a ND = non-detectable.

($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) (98%), sodium borohydride (NaBH_4) (98%), and hydrochloric acid (HCl) (36.5%) were obtained from Aldrich (St. Louis, MO). Sodium perchlorate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$) was purchased from EM Science (Cherry Hill, NJ). Micro-glass slides were from Corning Glass Works (Corning, NY). For substrate and solution preparations, deionized water (18.2 M Ω cm) was used throughout the experiment. All glassware was cleaned in a freshly prepared acid bath and rinsed thoroughly with deionized water prior to use.

Colloidal Au nanoparticles were prepared according to previously published methods.^{30,34} In brief, a “seed” colloidal suspension of Au was first prepared by mixing 1 mL of 1% aqueous $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 100 mL of H_2O with vigorous stirring for about 1 min, followed by sequential additions of 1 mL of 1% trisodium citrate and 1 mL of 0.075% NaBH_4 in 1% trisodium citrate. This seed Au suspension was stirred continuously for an additional 5 min and then stored at 4 °C. Au nanoparticles of ~ 54 nm in diameter were then prepared by heating 900 mL of dilute HAuCl_4 solution ($\sim 0.004\%$) to boiling, followed by the addition of 1 mL of the “seed” Au nanoparticles and 3.6 mL of a 1% trisodium citrate solution. The solution mixture was refluxed for an additional 10 min before it was cooled under stirring. The average size of synthesized Au nanoparticles (~ 54 nm) was determined by means of dynamic light scattering using a ZetaPlus particle size analyzer (Brookhaven Instruments, Holtsville, NY). Data were collected for every batch of the Au colloid at room temperature.

The DMAE-modified Au nanoparticles were prepared by adding 0.28 g DMAE into 400 mL of the above prepared Au colloid suspension, upon which the color of the Au colloids immediately turned from red to deep purple, suggesting the aggregation of Au nanoparticles by interacting with DMAE. The UV-visible spectrum showed a red shift in its primary absorption maxima from 525 to 790 nm, the latter of which is attributed to multipolar resonances of Au nanoparticles in higher-order coupled spheres.^{35,36} After mixing for approximately 5 h, the suspension was centrifuged at 14 000 rpm, and the concentrated Au nanoparticles were collected, washed with deionized water, and re-suspended in 0.01 M HCl solution (pH ~ 2) and used as a SERS substrate for perchlorate detection. This concentrated Au nanoparticle suspension was found to be stable for at least 8 months (after preparation), although ultrasonication is necessary to ensure well dispersed Au colloids before use.

For SERS analysis, the analyte ClO_4^- solution in the concentration range of 10^{-9} to 10^{-4} M was prepared by dilution in series (10 \times) from a stock solution of 10^{-3} M in deionized water. To evaluate potential matrix interferences from competing ions, measurements were also performed in a

synthetic groundwater (SGW) consisting of a mixture of SO_4^{2-} , PO_4^{3-} , and NO_3^- , each at 10^{-4} M, and Cl^- at 10^{-3} M. In addition, two contaminated groundwater samples (GW-1 and GW-2) were obtained from a field site in northern California and used for testing. Table I lists major anionic compositions and pH of the groundwater and SGW. The analyte, SGW, or GW samples (0.1 mL) were then mixed with 0.1 mL of the modified Au nanoparticle concentrate and 0.8 mL of water for analysis. A small drop (~ 10 μL) of the mixed suspension was placed on a glass slide and air-dried, and SERS spectra were collected after about 30 min.

Raman spectra were obtained using the Renishaw micro-Raman system equipped with a near-infrared diode laser at a wavelength of 785 nm for excitation (Renishaw Inc, New Mills, UK).^{26,27,30} The laser beam was set in position with a Leica Raman imaging microscope equipped with a 50 \times objective lens (0.5 numerical aperture) at a lateral spatial resolution of ~ 2 μm . The optics polarization was set perpendicular to the laser, and its intensity at the exit of the objective lens was ~ 1 mW by using a set of neutral density filters. A charge-coupled device (CCD) array detector was used to achieve signal detection from a 1200 grooves/mm grating light path controlled by Renishaw WiRE software and analyzed by Galactic GRAMS software.

RESULTS AND DISCUSSION

Quantitative Analysis of Perchlorate. Surface-enhanced Raman scattering spectra of perchlorate were first examined at concentrations ranging from 10^{-10} to 10^{-6} M in purified water, and each spectrum in Fig. 1A was offset for clarity. The primary Raman scattering peak (due to symmetric stretching vibration) of ClO_4^- occurred at about 934 cm^{-1} , which is consistent with literature data using both normal and surface-enhanced Raman spectroscopic techniques.^{25–27,29} The lowest ClO_4^- concentration detected was about 10^{-10} M, and a small ClO_4^- peak was visible (spectrum b). However, the detection limit was estimated at 10^{-9} M (or ~ 100 ng/L) with a signal-to-noise ratio greater than 3. These results suggest that the SERS technique was extremely sensitive to ClO_4^- through the use of DMAE-modified Au nanoparticle substrates. This detection limit is about two orders of magnitude lower than those reported recently by using either cystamine-modified gold nanoparticles²⁷ or positively charged silver nanoparticles sorbed with polyethyleneimine fragments (containing primary amino and amide functional groups).²⁹ These techniques give a relatively high background scattering resulting from complicated molecular structures of the organic modifiers (both cystamine and polyethyleneimine or its fragments).^{27,29} The background scattering in the spectral region between 900 and 950 cm^{-1} could interfere with the detection of ClO_4^- or overlap with the Raman band of ClO_4^- , especially at sub-micromolar concentration levels. On the other hand, no significant background Raman scattering was observed in the spectral region of ~ 890 – 960 cm^{-1} by using DMAE-modified Au nanoparticles as SERS substrates (Fig. 1A, spectrum a).

To our knowledge, this is the first time that DMAE has been used as a modifier for SERS detection of ClO_4^- . The rationale for using DMAE is based on the development of selective ion exchangers for ClO_4^- sorption, in which the selectivity is found to strongly depend on the charge and size of the quaternary alkyl-ammonium functional groups.^{3,37} The electrostatic attraction between ClO_4^- anions and positively

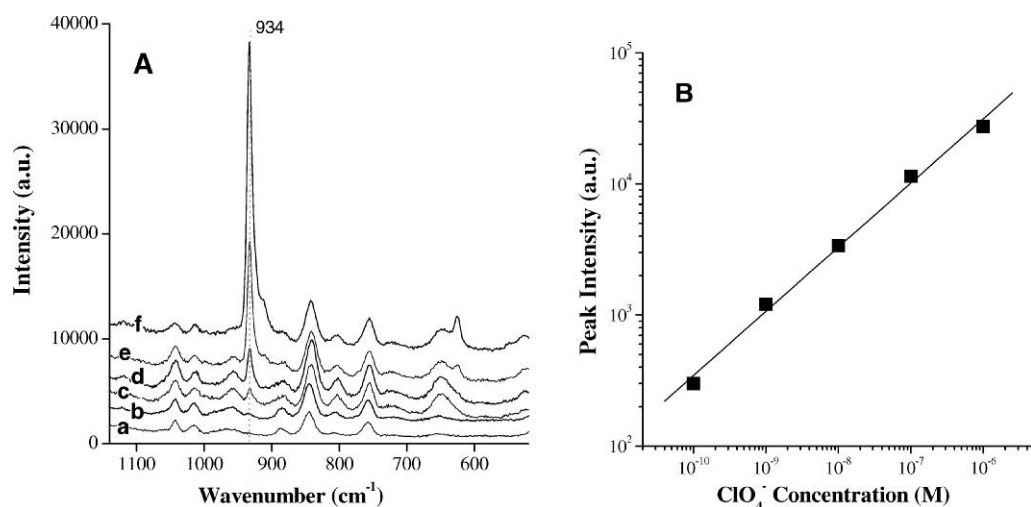


FIG. 1. (A) Raman spectroscopic analysis of ClO_4^- at concentrations of (a) 0, (b) 10^{-10} , (c) 10^{-9} , (d) 10^{-8} , (e) 10^{-7} , and (f) 10^{-6} M using DMAE-modified Au nanoparticles as a SERS substrate; (B) a log-log plot of the peak intensity at 934 cm^{-1} against the ClO_4^- concentration.

charged DMAE-modified Au nanoparticles enables a close contact and the concentration of ClO_4^- onto Au nanoparticle surfaces.^{26,27} Additionally, the amine functional groups could have facilitated the aggregation of Au nanoparticles, which is necessary to obtain strong electromagnetic plasmon enhancement on gold metal surfaces.^{21–23} Theoretical calculations have shown that the maximal SERS signal could be obtained when the analyte molecule is situated within the nanoneck regions of adjacent metal nanoparticles, where maximal electromagnetic field enhancement is achieved upon laser excitation.^{21,38} Therefore, the use of DMAE-modified Au SERS substrates offers advantages in sensitive detection of ClO_4^- in aqueous media. It yielded an enhancement factor of about 10^7 – 10^8 because, by using normal Raman spectroscopy (or without using Au nanoparticles), no Raman signal could be detected directly from the aqueous solution at perchlorate concentrations below 10^{-2} M.²⁷

Analysis of the spectra (Fig. 1A) also showed that the Raman band at 934 cm^{-1} increased consistently with an increase of aqueous ClO_4^- concentrations. A logarithm plot between the peak intensity and the ClO_4^- concentration yielded a linear relationship over a wide concentration range between 10^{-10} and 10^{-6} M (Fig. 1B). This observation is consistent with that observed for the detection of pertechnetate (TcO_4^-) ions by using similar techniques.³⁰ Sackmann and Materby also reported that the SERS intensity of adenine increased exponentially with its concentration when silver colloids were used as a SERS substrate.³³ These observations suggest that the technique could potentially be used as a quantitative or semi-quantitative tool for the analysis or rapid screening of perchlorate in aqueous media.

The surface modification of Au nanoparticles with DMAE enabled not only a high sensitivity but also a good reproducibility in detecting ClO_4^- in aqueous solution. The spot-to-spot reproducibility of Raman signal at 934 cm^{-1} was evaluated by randomly selecting about six spots under the microscope and measuring their corresponding SERS spectra (Fig. 2). Results indicate that all spectra virtually overlap (note that a small y-axis offset was used for clarity). The standard deviation of the peak intensity at 934 cm^{-1} was about 16% from these different spots. Similarly, the batch-to-batch

variations were found to be about $\pm 15\%$ when different batches of the modified Au nanoparticles were used. These observations are attributed to the fact that positively charged amine functional groups result in the sorption and thus an even distribution of ClO_4^- on Au nanoparticles. Also, as indicated earlier, the amine functional groups could have facilitated the aggregation of Au colloids, as evidenced by the self-assembly of DMAE-modified Au nanoparticles (Fig. 2, inset). Without surface modification, the analyte would be unlikely to be distributed evenly when it dries or crystallizes on metal nanoparticle surfaces (one of the contributing factors to observations of so-called “hot spots”). The probability of finding such hot spots is usually extremely low for detecting the target analyte.^{22,23} Nie and Emory have shown that about one in 100 to 1000 silver colloids are perhaps “hot” or SERS-active.²² This has been a major limiting factor for the use of SERS as a routine analytical tool. Therefore, techniques using

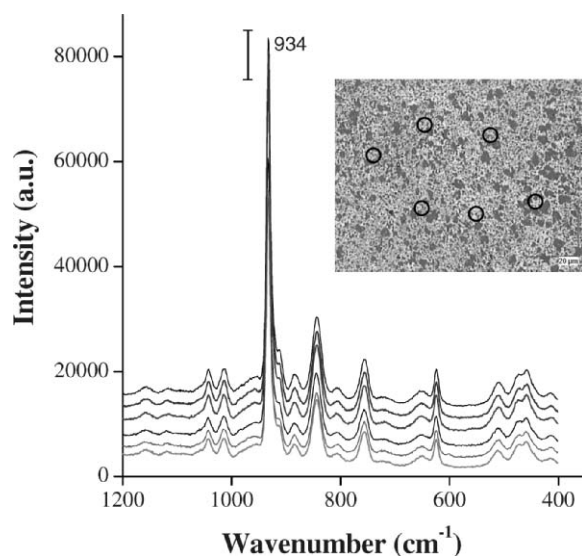


FIG. 2. SERS spectra of ClO_4^- (1×10^{-5} M) obtained from six randomly selected spots (inset) on a substrate made of DMAE-modified Au nanoparticles. Each spectrum was offset for clarity, and the error bar represents a standard deviation of about 16% at peak position 934 cm^{-1} .

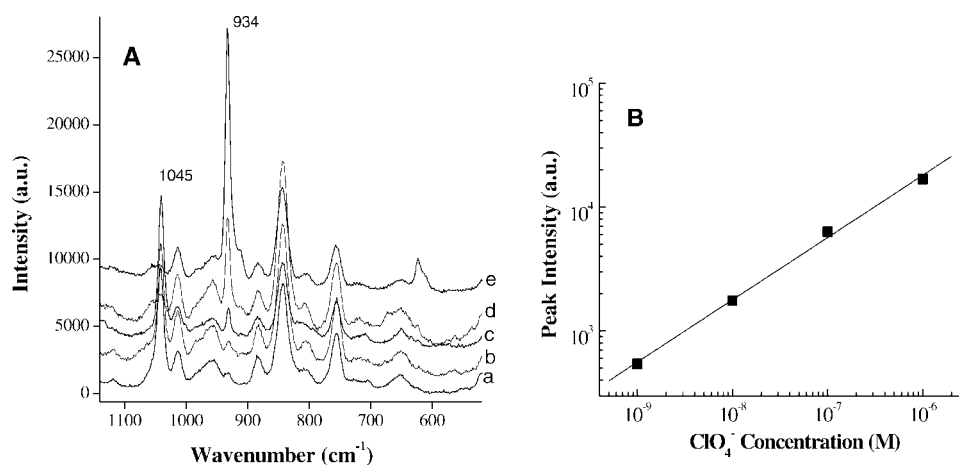


FIG. 3. (A) SERS spectroscopic analysis of ClO_4^- in the presence of background electrolytes of SO_4^{2-} , PO_4^{3-} , and NO_3^- at 10^{-4} M each, and Cl^- at 10^{-3} M. Perchlorate concentrations varied from (a) 0, (b) 10^{-9} , (c) 10^{-8} , (d) 10^{-7} , to (e) 10^{-6} M. (B) A log-log plot of the peak intensity at 934 cm^{-1} against the ClO_4^- concentration.

surface modified Au nanoparticles as SERS substrates offer clear advantages here for detecting ClO_4^- with improved sensitivity and reproducibility.^{29,30}

Analysis of Perchlorate in Contaminated Samples. To assess the potential interferences in the quantitative analysis of ClO_4^- in realistic contaminated water samples, we further examined the detection of ClO_4^- in the presence of orders of magnitude higher concentrations of background electrolytes including SO_4^{2-} , PO_4^{3-} , and NO_3^- , each at 10^{-4} M, and Cl^- at 10^{-3} M. The resulting SERS spectra are shown in Fig. 3A. In comparison with those shown in Fig. 1A, the general features of the spectra remain unchanged with the exception of the band at 1045 cm^{-1} (Fig. 3A), which was assigned to the stretching vibration of the NO_3^- ion. However, we note that the peak intensity at 1045 cm^{-1} decreased considerably with increasing concentrations of ClO_4^- in solution, especially at concentrations of 10^{-7} and 10^{-6} M. These observations suggest possible competitive interactions between ClO_4^- and NO_3^- ions for sorption onto the Au nanoparticle substrate. The fact that the nitrate band at 1045 cm^{-1} was substantially suppressed could be attributed to the preferential sorption of ClO_4^- ions because of limited sorption sites on DMAE-modified Au nanoparticles. Similar observations have been reported when cystamine-modified gold nanoparticles were used for the detection of ClO_4^- and NO_3^- .²⁷

Although SO_4^{2-} and PO_4^{3-} show vibrational bands at about 980 and 925 cm^{-1} , respectively,³⁹ their Raman scattering apparently was not enhanced by using DMAE-modified Au nanoparticles as a SERS substrate and thus did not significantly interfere with the detection of ClO_4^- ions (Fig. 3). These results suggest that the SERS substrate enhanced the Raman scattering only for some selected anionic species, although exact mechanisms by which the Raman scattering of different ions or molecules is selectively enhanced remain a subject of intensive investigation.^{21–24,27,39} One possible explanation is that SO_4^{2-} and PO_4^{3-} ions are only weakly sorbed on the SERS substrate because of their relatively high hydration energy as compared with that of the ClO_4^- ion.³ However, we note that the presence of these background ionic species did cause overall decreased peak intensities at 934 cm^{-1} for perchlorate. For example, at the ClO_4^- concentration of 10^{-6} M, its peak intensity decreased about 35% as compared with

that measured in deionized water (Fig. 1A). Such a decrease in peak intensities of ClO_4^- can be expected because of the presence of 2 to 5 orders of magnitude higher concentrations of background ionic species (NO_3^- , SO_4^{2-} , PO_4^{3-} , Cl^-), which may compete for interactions with the SERS substrate and thus reduce the scattering signal of perchlorate. On the other hand, the presence of these background electrolytes did not appear to impact the quantitative analysis of perchlorate, and a plot of the peak intensity (at 934 cm^{-1}) and the ClO_4^- concentration yielded a linear relationship on a log scale (Fig. 3B). These results again indicate that the DMAE-modified Au SERS substrates could be used for quantitative or semi-quantitative analysis of ClO_4^- in aqueous media. The technique has the potential to be used as a rapid screening tool for environmental analysis because portable Raman spectrometers are readily available and relatively inexpensive.

We further analyzed two contaminated groundwater samples obtained from a field site in Northern California. The groundwater GW-1 contained a ClO_4^- concentration of 8.3×10^{-6} M, which is about three orders of magnitude lower than the concentration of competing ions listed in Table I. The other sample (GW-2) had a ClO_4^- concentration of 1×10^{-8} M, which is five to six orders of magnitude lower than the concentration of competing ions in the water. These samples were analyzed as is or diluted 10 times with deionized water, and the results are shown in Fig. 4. Using Fig. 3B as the standard calibration curve, the calculated ClO_4^- concentrations were 7.86×10^{-6} and 1.02×10^{-8} M for undiluted GW-1 and GW-2 samples, respectively.

These data are in good agreement with those obtained using ion chromatography, which were 8.3×10^{-6} and 1×10^{-8} M (Table I). However, for 10 \times diluted samples, the SERS analysis substantially overestimated the ClO_4^- concentrations, which were 3.43×10^{-5} and 1.15×10^{-8} M for the GW-1 and GW-2 samples. These observations are not surprising because the background electrolyte concentrations in diluted samples were substantially lower than those used in the calibration “standards” (Fig. 3B). As a result, an increased SERS signal was observed for ClO_4^- because of fewer matrix interferences in the diluted samples. However, by using the calibration curve in Fig. 1B (in deionized water), the calculated ClO_4^-

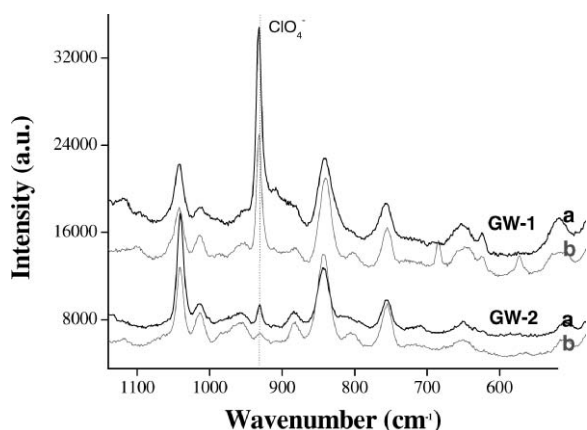


FIG. 4. SERS spectra of two contaminated groundwater samples (GW-1 and GW-2) (a) without dilution or (b) with a 10 \times dilution. The ClO_4^- concentrations in undiluted GW-1 and GW-2 were 8.3×10^{-6} and 1×10^{-8} M (Table I).

concentration in GW-1 was 1.08×10^{-5} M, which is close to its true value measured using ion chromatography.

These results emphasize the need to prepare samples and reference standards in the same or similar matrices, as a common practice used in any quantitative analysis. For practical applications, future studies and validation will be needed in order to cover a wide variety of environmental conditions for perchlorate detection; standard addition techniques may be used to correct matrix interferences and thus to ensure good reproducibility in quantitative analysis.

ACKNOWLEDGMENTS

This research was supported in part by the Strategic Environmental Research and Development Program (SERDP) of the U.S. Department of Defense and the Laboratory Directed Research and Development Program of the Oak Ridge National Laboratory, which is managed by UT-Battelle, LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725.

1. P. Damian and F. W. Pontius, *Environ. Prot.* **10**, 24 (1999).
2. E. T. Urbansky, B. Gu, M. L. Magnuson, G. M. Brown, and C. A. Kelty, *J. Sci. Food Agric.* **80**, 1798 (2000).
3. B. Gu and J. D. Coates, *Perchlorate Environmental Occurrence, Interactions and Treatment* (Springer, New York, 2006).
4. B. C. Blount, L. Valentin-Blasini, J. D. Osterloh, J. P. Mauldin, and J. L. Pirkle, *J. Exp. Sci. Environ. Epidemiol.* **17**, 400 (2007).
5. W. A. Jackson, P. Joseph, P. Laxman, K. Tan, P. N. Smith, L. Yu, and T. A. Anderson, *J. Agric. Food Chem.* **53**, 369 (2005).

6. A. B. Kirk, P. K. Martinelango, K. Tian, A. Dutta, E. E. Smith, and P. K. Dasgupta, *Environ. Sci. Technol.* **39**, 2011 (2005).
7. C. A. Sanchez, K. S. Crump, R. I. Krieger, N. R. Khandaker, and J. P. Gibbs, *Environ. Sci. Technol.* **39**, 9391 (2005).
8. L. Valentin-Blasini, J. P. Mauldin, D. Maple, and B. C. Blount, *Anal. Chem.* **77**, 2475 (2005).
9. W. Bao and B. Gu, *Environ. Sci. Technol.* **38**, 5073 (2004).
10. J. K. Böhlke, N. C. Sturchio, B. Gu, J. Horita, G. M. Brown, W. A. Jackson, and J. R. Batista, *Anal. Chem.* **77**, 7838 (2005).
11. N. C. Sturchio, J. K. Böhlke, A. D. Beloso, S. H. Stieger, L. J. Heraty, and P. B. Hatzinger, *Environ. Sci. Technol.* **41**, 2796 (2007).
12. W. A. Jackson, S. K. Anandam, T. Anderson, T. Lehman, K. Rainwater, S. Rajagopalan, M. Ridley, and R. Tock, *Ground Water Monitoring Remediation* **25**, 137 (2005).
13. P. K. DasGupta, J. V. Dyke, A. B. Kirk, and W. A. Jackson, *Environ. Sci. Technol.* **40**, 6608 (2006).
14. P. K. Dasgupta, P. K. Martinelango, W. A. Jackson, T. A. Anderson, K. Tian, R. W. Tock, and S. Rajagopalan, *Environ. Sci. Technol.* **39**, 1569 (2005).
15. E. T. Urbansky, *Bioremed. J.* **2**, 81 (1998).
16. P. E. Jackson, S. Gokhale, T. Streib, J. S. Rohrer, and C. A. Pohl, *J. Chromatogr. A* **888**, 151 (2000).
17. E. T. Urbansky, *Crit. Rev. Anal. Chem.* **30**, 311 (2000).
18. R. Perez-Olmos, A. Rios, M. P. Martin, R. A. S. Lapa, and J. L. F. C. Lima, *Analyst (Cambridge, U.K.)* **124**, 97 (1999).
19. C. Sanchez-Pedreno, J. A. Ortuno, and J. Hernandez, *Anal. Chim. Acta* **415**, 159 (2000).
20. S. W. Park, K. H. Jin, J. H. You, T. J. Kim, K. J. Paeng, and K. H. Kong, *Anal. Sci.* **13**, 243 (1997).
21. K. Zhao, H. Xu, B. Gu, and Z. Zhang, *J. Chem. Phys.* **125**, 081102 (2006).
22. S. Nie and S. R. Emory, *Science (Washington, D.C.)* **275**, 1102 (1997).
23. K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari, and M. S. Feld, *Chem. Rev.* **87**, 2957 (1999).
24. C. M. Ruan, W. Wang, and B. Gu, *J. Raman Spectrosc.* **38**, 568 (2007).
25. P. A. Mosier-Boss and S. H. Lieberman, *Appl. Spectrosc.* **57**, 1129 (2003).
26. B. Gu, J. Tio, W. Wang, Y. Ku, and S. Dai, *Appl. Spectrosc.* **58**, 741 (2004).
27. C. M. Ruan, W. Wang, and B. Gu, *Anal. Chim. Acta* **567**, 114 (2006).
28. W. Wang, C. M. Ruan, and B. Gu, *Anal. Chim. Acta* **567**, 121 (2006).
29. S. Tan, M. Erol, A. Attygalle, H. Du, and S. Sukhishvili, *Langmuir* **23**, 9836 (2007).
30. B. Gu and C. M. Ruan, *Anal. Chem.* **79**, 2341 (2007).
31. C. M. Ruan, W. Wang, and B. Gu, *Anal. Chim. Acta* **605**, 80 (2007).
32. W. Wang and B. Gu, *Appl. Spectrosc.* **59**, 1509 (2005).
33. M. Sackmann and A. Materny, *J. Raman Spectrosc.* **37**, 305 (2006).
34. L. G. Olson, Y. S. Lo, T. P. Beebe, and J. M. Harris, *Anal. Chem.* **73**, 4268 (2001).
35. C. S. Weisbecker, M. V. Merritt, and G. M. Whitesides, *Langmuir* **12**, 3763 (1996).
36. Z. Y. Zhong, S. Patskovskyy, P. Bouvrette, J. H. T. Luong, and A. Gedanken, *J. Phys. Chem. B* **108**, 4046 (2004).
37. B. Gu, G. M. Brown, and C. C. Chiang, *Environ. Sci. Technol.* **41**, 6277 (2007).
38. H. Xu, J. Aizpura, M. Kall, and P. Apell, *Phys. Rev. E* **62**, 4318 (2000).
39. G. Niaura and R. Jakubenas, *J. Electroanal. Chem.* **510**, 50 (2001).